

# Electronic properties of curved graphene sheets

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A model is proposed to study the electronic structure of slightly curved graphene sheets with an arbitrary number of pentagon-heptagon pairs and Stone-Wales defects based on a cosmological analogy. The disorder induced by curvature produces characteristic patterns in the local density of states that can be observed in scanning tunnel and transmission electron microscopy.

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The recent synthesis of single or few layers of graphite[1, 2] allows to test the singular transport properties predicted in early theoretical studies[3, 4, 5, 6] and experiments[7]. The discovery of a substantial field effect [8] and of ferromagnetic behavior[9] allows to envisage graphene as a reasonable replacement of nanotubes in electronic applications. Disorder plays a very important role in the electronic properties of low dimensional materials.

Substitution of an hexagon by an  $n$ -sided ring in the hexagonal lattice without affecting the threefold coordination of the carbon atoms leads to the warping of the graphene sheet. Rings with  $n > 6$  ( $n < 6$ ), induce locally positive (negative) curvature. Inclusion of an equal number of pentagons and heptagonal rings would keep the flatness of the sheet at large scales and produce a flat structure with curved portions that would be structurally stable and have distinct electronic properties. This defects give rise to long range modifications in the electronic wave function that affect the electronics in a way different from that produced by vacancies or other impurities modelled by local potentials. Pentagon-heptagon pairs and Stone-Wales defects made of two adjacent heptagons and two pentagons form naturally in experiments of ion bombarded nanotubes as a mechanism to reduce the dangling bonds in large vacancies[10] and have been observed to form in situ in single graphene layers by high-resolution transmission electron microscopy (TEM)[11].

We propose a method, based on a cosmological analogy, to compute the electronic structure and transport properties of curved graphene sheets consisting of an arbitrary number of topological defects located at fixed positions of the lattice. We see that, unlike vacancies and voids, the combination of positive and negative curvature gives rise to characteristic inhomogeneous patterns in the density of states that affect the transport properties of the layers and can be observed in scanning tunnel (STM) and electron transmission spectroscopy (ETS). The present analysis can help in the experimental characterization of graphene samples and in the correct analysis of STM images. The results obtained can be related to recent Electrostatic Force Microscopy (EFM) measurements that indicate large potential differences between

micrometer large regions on the surface of highly oriented graphite[12] and to the suppression of magnetoresistance in single layered graphene reported in [13]. We apply the formalism to present the corrections to the local density of states induced by pentagon-heptagon pairs and Stone-Wales defects in the average planar graphene sheet.

*Description of the model.* The conduction band of graphene is well described by a tight binding model which includes the  $\pi$  orbitals which are perpendicular to the plane at each C atom[14, 15]. This model describes a semimetal, with zero density of states at the Fermi energy, and where the Fermi surface is reduced to two inequivalent K-points located at the corners of the hexagonal Brillouin Zone. The low-energy excitations with momenta in the vicinity of any of the Fermi points  $K_{\pm}$  have a linear dispersion and can be described by a continuous model which reduces to the Dirac equation in two dimensions[16, 17, 18]. In the absence of interactions or disorder mixing the two Fermi points the electronic properties of the system are well described by the effective low-energy Hamiltonian:

$$\mathcal{H}_{0\pm} = i\hbar v_F(\sigma_x \partial_x \pm \sigma_y \partial_y), \quad (1)$$

where  $\sigma_{x,y}$  are the Pauli matrices,  $v_F = (3ta)/2$ , and  $a = 1.4\text{\AA}$  is the distance between nearest carbon atoms. The components of the two-dimensional spinor:  $\bar{\Psi}_i(\mathbf{r}) = (\varphi_A(\mathbf{r}), \varphi_B(\mathbf{r}))_i$  correspond to the amplitude of the wave function in each of the two sublattices (A and B) which build up the honeycomb structure. Pentagons and heptagons can be viewed as disclinations in the graphene lattice, and, when circling one such defect, the two sublattices in the honeycomb structure as well as the two Fermi points are exchanged. The scheme to incorporate this change in a continuous description was discussed in refs. [16, 17] and [19]. The process can be described by means of a non Abelian gauge field, which rotates the spinors in the flavor space of the Fermi points. The two spinors associated to each Fermi point can be combined into a four component Dirac spinor  $\bar{\Psi}(\mathbf{r}) = (\bar{\Psi}_+(\mathbf{r}), \bar{\Psi}_-(\mathbf{r}))$  which in the presence of a single disclination is an eigenstate of the Hamiltonian[20]

$$H = -iv_F \vec{\gamma} \cdot \vec{\partial} + g\gamma^q \vec{\gamma} \cdot \vec{A}(\mathbf{r}). \quad (2)$$

$v_F$  is the Fermi velocity,  $\gamma^i$  are  $4 \times 4$  matrices constructed from the Pauli matrices,  $\gamma^q = \frac{\sigma^q}{2} \otimes I$ , the latin indices run over the two spatial dimensions and  $g$  is a coupling parameter related to the deficit angle of the defect.

We use time-independent perturbation theory to calculate corrections to the self-energy in the weak coupling regime of the parameter  $\hat{g} \equiv \frac{\Phi}{2\pi L^2}$ , where the constant  $\Phi$  is the strength of the vortex:  $\Phi = \oint \vec{A} d\vec{r}$  related to the opening angle of the defect by  $\Phi = (1 - b)$ .  $L$  is the dimension of the sample.

In a disordered system, in general, because of the presence of an external potential or impurities, the space is inhomogeneous. The Green's function doesn't depend on the difference  $(\mathbf{r} - \mathbf{r}')$  and  $\mathbf{k}$  is no longer a good quantum number. If the external potential or the effect of the impurities are time-independent we have elastic scattering and the states  $\mathbf{k}$  and  $\mathbf{k}'$  have the same energy. We want to calculate the total density of states  $\rho(\omega)$  of the system perturbed by the defect via the vector potential given in eq. (2). This density is the imaginary part of the Green's function integrated over all positions, in the limit  $\mathbf{r}' \rightarrow \mathbf{r}$ :

$$\rho(\omega) = \int \text{Im} G(\omega, \mathbf{r}, \mathbf{r}) d\mathbf{r}.$$

In terms of the Green's function in momentum representation,  $\rho(\omega)$  can be written as:

$$\rho(\omega) = \text{Im} \int \int \frac{d\mathbf{k}}{(2\pi)^2} \int \frac{d\mathbf{k}'}{(2\pi)^2} e^{i\mathbf{k}\mathbf{r}} e^{-i\mathbf{k}'\mathbf{r}} G(\omega, \mathbf{k}, \mathbf{k}') d\mathbf{r}.$$

The integration over  $\mathbf{r}$  gives delta function  $4\pi^2 \delta(\mathbf{k} - \mathbf{k}')$ , and  $\rho(\omega)$  then reads:

$$\rho(\omega) = \int \frac{d\mathbf{k}}{(2\pi)^2} \text{Im} G(\omega, \mathbf{k}, \mathbf{k}).$$

*Generalization to negative curvature and an arbitrary number of defects.* An alternative approach to the gauge theory of defects is to include the local curvature induced by an  $n$ -membered ring by coupling the Dirac equation to a curved space. This approach was introduced in [16, 17] to study the electronic spectrum of closed fullerenes and has recently been used for fullerenes of different shapes in [21]. The holonomy discussed in the gauge approach is included in the formalism by means of the spin connection[22]. In most of the previous works in this context, the graphene sheet was wrapped on a geometrical surface that can be easily parametrized. The situation is more complicated if we try to describe the samples that are being obtained in the laboratory that are flat sheets with local corrugation[13].

In this context one can see that the substitution of an hexagon by a polygon of  $n < 6$  sides gives rise to a conical singularity with deficit angle  $(2\pi/6)(6 - n)$ . This kind of singularities have been studied in cosmology as they are produced by cosmic strings, a type of topological defect that arises when a  $U(1)$  gauge symmetry is spontaneously broken[23]. We can obtain the correction to the density of

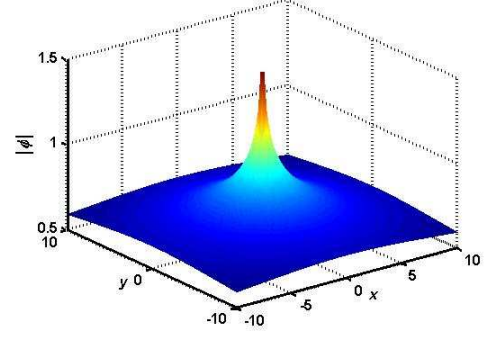


FIG. 1: Electronic density around a conical defect.

states induced by a set of defects with arbitrary opening angle by coupling the Dirac equation to a curved space with an appropriate metric as described in ref. [24]. The metric of a two dimensional space in presence of a single cosmic string in polar coordinates is:

$$ds^2 = -dt^2 + dr^2 + c^2 r^2 d\theta^2, \quad (3)$$

where the parameter  $c$  is a constant related to the deficit angle by  $c = 1 - b$ .

The dynamics of a massless Dirac spinor in a curved spacetime is governed by the Dirac equation:

$$i\gamma^\mu \nabla_\mu \psi = 0 \quad (4)$$

The difference with the flat space lies in the definition of the  $\gamma$  matrices that satisfy generalized anticommutation relations

$$\{\gamma^\mu, \gamma^\nu\} = 2g^{\mu\nu}, \quad (5)$$

where  $g_{\mu\nu}$  is given by (3), and in the covariant derivative operator, defined as

$$\nabla_\mu = \partial_\mu - \Gamma_\mu \quad (6)$$

where  $\Gamma_\mu$  is the spin connection of the spinor field that can be calculated using the tetrad formalism[25]. Fig. 1 shows the solution of the Dirac equation (4) in the presence of a single defect with a positive deficit angle (positive curvature). The electronic density is strongly peaked at the position of the defect suggesting a bound state but the behavior at large distances is a power law with an angle-dependent exponent less than two which corresponds to a non normalizable wave function. This behavior is similar to the one found in the case of a single vacancy[26] and suggests that a system with a number of this defects with overlapping wave functions will be metallic.

The case of a single cosmic string which represents a deficit angle in the space can be generalized to describe seven membered rings representing an angle surplus by considering a value for the deficit angle  $c$  greater than 1.

This situation is non-physical from a general relativity viewpoint as it would correspond to a string with negative mass density but it makes perfect sense in our case. The scenario can also be generalized to describe an arbitrary number of pentagons and heptagons by using the following metric:

$$ds^2 = -dt^2 + e^{-2\Lambda(x,y)}(dx^2 + dy^2), \quad (7)$$

where  $\Lambda(\mathbf{r}) = \sum_{i=1}^N 4\mu_i \log(r_i)$  and  $r_i = [(x - a_i)^2 + (y - b_i)^2]^{1/2}$ . This metric describes the space-time around  $N$  parallel cosmic strings, located at the points  $(a_i, b_i)$ . The parameters  $\mu_i$  are related to the angle defect or surplus by the relationship  $c_i = 1 - 4\mu_i$  in such manner that if  $c_i < 1 (> 1)$  then  $\mu_i > 0 (< 0)$ .

From equation (4) we can write down the Dirac equation for the electron propagator,  $S_F(x, x')$ :

$$i\gamma^\mu(\partial_\mu - \Gamma_\mu)S_F(x, x') = \frac{1}{\sqrt{-g}}\delta^3(x - x'), \quad (8)$$

where  $x = (t, \mathbf{r})$ . The local density of states  $N(\omega, \mathbf{r})$  is obtained from (8) by Fourier transforming the time component and taking the limit  $\mathbf{r} \rightarrow \mathbf{r}'$ :

$$N(\omega, \mathbf{r}) = \text{ImTr}S_F(\omega, \mathbf{r}, \mathbf{r}). \quad (9)$$

We solve eq. (9) considering the curvature induced by the defects as a perturbation of the flat graphene layer. The details of the calculation will be given elsewhere[20]. Here we will show the results obtained.

*Results.* Fig. 2 shows the correction to the local density of states at energy  $w = 2.1\text{eV}$  and for a large region of the graphene plane with a pentagon (p)-heptagon (h) pair located out of plane at  $p = [-0.3, -5]$ ,  $h = [0.3, -5]$ . The LDOS is normalized with the clean DOS of graphene at the given energy. The color code is indicated in the figure: green stands for the DOS of perfect graphene at the given energy and red (blue) indicates an accumulation (depletion) of the density in the area. The correction obtained is of the order of a few percent. We can see that pentagonal (heptagonal) rings enhance (depress) the electron density. A similar result has been obtained in [27] with numerical simulations. It is to note that a somehow contradictory result was obtained in [28] where they studied the electrostatics of a graphene plane with defects. They found that disclinations corresponding to rings with more (less) than six carbon atoms function as attractors (repellent) to point charges. It is obvious that this issue needs further investigation. The dipolar character of the defect is clear from the figure and makes this type of defects unique. The effects produced will extend spatially much beyond the scale of the defect what can be related with recent Electrostatic Force Microscopy (EFM) measurements that indicate large potential differences between micrometer large regions on the surface of highly oriented graphite that do not show inhomogeneities in STM[12]. The interference patterns in the DOS depend on the position and on the relative

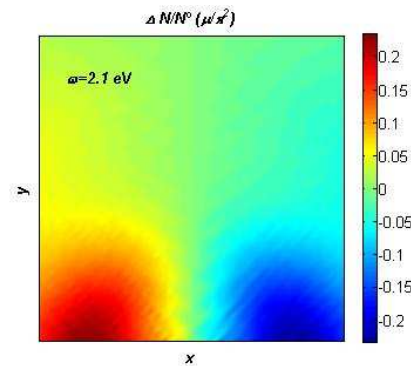


FIG. 2: (Color online) Image of the correction to the local density of states in a large portion of the plane with a heptagon-pentagon pair located out of plane at position  $[0.3, -5]$ ,  $[-0.3, -5]$ .

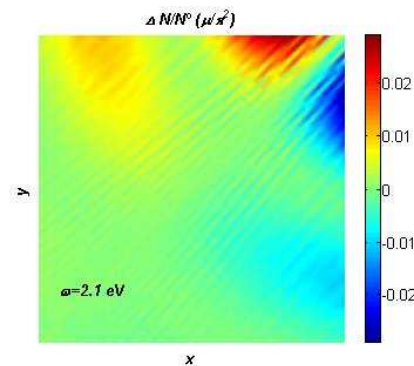


FIG. 3: (Color online) Correction to the local density of states around a Stone-Wales defect located out of the image in the upper right corner.

orientation of the dipoles. Fig. 3 shows the patterns produced by a Stone-Wales defect (two pairs of pentagons ( $p_i$ ) heptagons ( $h_i$ )) located out of plane at positions  $p_1 = [5, 5.6]$ ,  $p_2 = [6.5, 6]$ ,  $h_1 = [6, 5.5]$ ,  $h_2 = [6, 6.9]$  for a frequency  $w = 2.1\text{eV}$ .

*A random distribution of defects.* A random distribution of topological defects can be described in the continuous model by a (non abelian) random gauge field. The disorder is defined by a single dimensionless quantity,  $\Delta$ , which is proportional to the average fluctuations of the field:

$$\langle \tilde{\mathbf{A}}(\tilde{\mathbf{r}})\tilde{\mathbf{A}}(\tilde{\mathbf{r}}') \rangle = \Delta\delta^2(\tilde{\mathbf{r}} - \tilde{\mathbf{r}}') \quad (10)$$

The statistical properties of the gauge field induced by topological defects were analyzed in ref. [19] following a renormalization group scheme and a complete phase diagram as a function of disorder and Coulomb interaction was obtained in [29].

In ref. [19] it was shown that when pentagons and heptagons are bound in dislocations with average distance  $b$ ,

the vector field of a vortex-antivortex dipole decays as  $r^{-2}$  and the behavior of  $\Delta$  was found to be:

$$\Delta \propto \Phi_0^2 n b^2 \quad (11)$$

where  $n$  is the density of dislocations.

Assuming that random fields induced by topological defects have the same statistical properties to those with gaussian disorder with the same value of  $\Delta$ , a renormalization group (RG) analysis using the replica trick gives rise to an effective interaction between fermion fields in different replicas. The resulting self-energy is logarithmically divergent what can be interpreted as a renormalization of the density of states[19]. The results obtained in this paper show a qualitative picture of the corrected DoS. The influence of these defects on the localization in graphene has been analyzed recently in [30].

The type of disorder analyzed in this article belongs to the random gauge field in the classification of [29]. There it was shown that the combination of this type of disorder with the unscreened Coulomb interaction give rise to a line of infrared stable fixed points. Topological defects give rise also to long range correlated disorder whose properties will be analyzed elsewhere[20].

*Conclusions and open problems.* We have presented in this article results on the electronic structure of a curved graphene sheet with pentagon-heptagon pairs that we expect to be present in the samples that are subject of present investigation. The formalism can also apply to clean samples of graphite showing strong anisotropy and

to curved samples of graphene with an arbitrary number of defects with any sign of the curvature. The model can also be used to study transport properties of the curved graphene sheets and of nanographite and results will be presented in [20]. The main achievement of this paper is the proposal of a formalism that can describe the corrugations observed in the experiments and predicts charge inhomogeneities that can be used to characterize the samples. We have computed the local density of states with the geometrical formalism found that it is enhanced around defects which induce positive curvature in the lattice while the charge is "repelled" from regions with negative curvature. Heptagon-pentagon pairs that keep the graphene sheet flat in the long range behave as dipoles and give rise to characteristic modulations of the DOS that can be observed by STM and can explain recent experiments. The magnitude of the oscillations increases with the frequency and the characteristic patterns could be used to characterize the graphene samples. The features predicted in this work should also be observable in other layered materials with similar structure as boron nitride[31]. The present analysis can help to clarify the issue of the analysis and interpretation of STM images.

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